There is some additional support for the idea of a weak chloride complex of Pu(III). From partition measurements, Reas[18] found 66% of Pu(IV) to be complexed by chloride in 1 *M* hydrochloric acid at 25°. From the Pu(III)–Pu(IV) e.m.f. measurements the percentage Pu(IV) complexed is only *ca.* 40%, if it is assumed that Pu(III) is itself not complexed. If, however, the same degree of complexing is assumed for Pu(III) as for lanthanum, the complexing of Pu(IV) becomes approximately 60%, which is in good agreement with Reas' value.

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[18] W. H. Reas, unpublished work, this Laboratory.

NOTES

Absorption Spectra of Some α- and β-Diketones[1,2]

BY R. PERCY BARNES AND GLADYS ESTELLE PINKNEY

RECEIVED AUGUST 4, 1952

Several α- and β-diketones have been studied spectroscopically. In carbon tetrachloride solutions the enols of the α-diketones are unchelated while the enols of the β-diketones have a chelated structure.

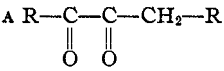
Many investigators have studied β-diketones from the standpoint of structure. Hilbert and co-workers[3] studied acetylacetone, benzoylacetone, and dibenzoylmethane and found no characteristic OH absorption for these β-diketones which fulfill the geometric requirements for chelated six-membered rings. Compounds were studied also which if chelated would give rise to five- or seven-membered rings. They showed characteristic OH absorption.

On the other hand, Morton and co-workers[4] concluded that dibenzoylmethane exists as the unchelated enol. Henecka[5] supports the chelated structure of the enol. In his review he points out that the enol is less soluble in polar media, contrary to what one would expect. The basis for the reverse behavior is that the chelate is formed, thereby tying-up the OH in the ring.

We decided to study a number of β-diketones in the 3 and 6 μ regions of the spectra. However, we considered it best to study a number of α-diketones first which if chelated would result in five-membered rings. That this would be unlikely[3] was supported also by Kohler and Barnes[6] who found in studying phenylbenzylglyoxal that upon distillation of the α-diketone, the distillate was rich in the keto form which is evidence against chelation.

The following α-diketones were studied in 0.01 molar solutions with carbon tetrachloride as the solvent. The curves were run from two to seven microns.

TABLE I

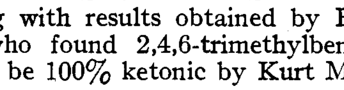
GENERAL FORMULA 

$R-\overset{\overset{}{}}{\underset{\|}{C}}-C-CH_2-R^1$

$R-C(=O)-C(=O)-CH_2-R^1$

I, R and R¹ = phenyl
II, R = mesityl; R¹ = phenyl
III, R = nitromesityl; R¹ = phenyl
IV, R = dinitromesityl; R¹ = phenyl
V, R = mesityl; R¹ = *m*-nitrophenyl
VI, R = mesityl; R¹ = *p*-methoxyphenyl
VII, R = phenyl; R¹ = mesityl

In compounds I through VI we found absorption bands at 2.95 μ and 6 μ which are the regions of OH and carbonyl absorption, respectively, and also bands at 3.5 μ and 6.25 μ indicating CH and phenyl absorption, respectively. These results indicate that diketones I through VI exist as unchelated enols.



The fact that they do not form five-membered ring chelates is in keeping with Hilbert's[3] and Kohler's[6] findings.

Diketone VII was found to have no band at 2.95 μ. A new band appeared at 5.85 μ and the bands at 3.5, 6.25 and 6 μ remained. This indicates that diketone VII exists in the ketonic form, in keeping with results obtained by Barnes and Brown[7] who found 2,4,6-trimethylbenzylphenylglyoxal to be 100% ketonic by Kurt Meyer titration.

The disappearance of the OH band alone would not indicate chelation since the carbonyl bands would disappear also, because they as well as the OH would be tied-up in the ring.

We then turned our attention to the following β-diketones which were measured in 0.04 molar carbon tetrachloride solutions in the 2–7 μ region.

Diketones VIII through XIII did not exhibit absorption at 2.95, 6 and 5.85 μ, indicating that they are neither unchelated enols nor diketones.

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[1] This work was supported by a grant from the Research Corporation of New York for the purchase of a Perkin-Elmer 12 C infrared spectrometer.

[2] The authors wish to acknowledge the invaluable aid of Mr. Jonas Carroll of the Food and Drug Administration, Federal Security Agency, and the use of their Perkin-Elmer 21 infrared spectrometer.

[3] G. E. Hilbert, O. R. Wulf, S. B. Hendricks and M. Liddel, THIS JOURNAL, 58, 548 (1936).

[4] R. A. Morton, A. Hassan and T. C. Calloway, *J. Chem. Soc.*, 900 (1934).

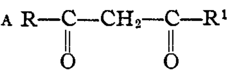
[5] H. Henecka, "Chemie der Beta-Dicarbonyl-Verbindungen," Springer Verlag, Berlin-Gottingen-Heidelberg, 1950.

[6] E. P. Kohler and R. P. Barnes, THIS JOURNAL, 56, 211 (1934).

[7] R. Percy Barnes and Robert J. Brown, *ibid.*, 65, 412 (1943).

TABLE II

GENERAL FORMULA

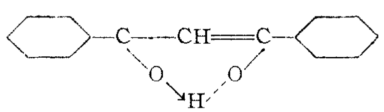


$\mathrm{R-\underset{\underset{O}{\|}}{C}-CH_2-\underset{\underset{O}{\|}}{C}-R^1}$

VIII, R and R^1 = phenyl
IX, R = *p*-bromophenyl; R^1 = phenyl
X, R = phenyl; R^1 = mesityl
XI, R = *p*-methoxyphenyl; R^1 = mesityl
XII, R = *m*-nitrophenyl; R^1 = mesityl
XIII, R = *p*-nitrophenyl; R^1 = mesityl

These β-diketones like the α-diketones did exhibit absorption at 3.4 and 6.25 μ which is characteristic of CH and phenyl absorption.

Thus we have negative evidence, the disappearance of bands at 2.95 and 6 μ, for the chelated structure of the β-ketones. It is difficult to indicate the presence of the O–H–O band since it too absorbs at about 3.4 μ.



However, the O–D–O band[8] appears at about 4.35 μ, and it is the plan of the authors to prepare β-diketones with the labile hydrogen replaced by deuterium and study them spectroscopically in an attempt to establish definitely that the enols of the β-diketones are chelated.

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(8) R. C. Herman and R. Hofstadter, *J. Chem. Phys.*, **6**, 534 (1938).

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Boiling Point and Composition of Methanethiol–Isobutane Azeotrope

BY F. R. BROOKS AND A. C. NIXON

RECEIVED AUGUST 18, 1952

Recently Denyer, Fidler and Lowry[1] predicted the boiling point and composition of an azeotrope between methanethiol and isobutane by extrapolation from the boiling points and azeotropic compositions of other thiols and hydrocarbons. We recently had occasion to determine the boiling point of this azeotrope and find that the azeotrope has a boiling point of −13.0° and contains 17.5 mole % of the thiol; corresponding values of −16.5° and 12.5 mole % were predicted by Denyer, *et al.* The difference between the observed and predicted values may reflect the deviation which commonly occurs with the first member of a series or it may be due to uncertainty in our determination. Our data were obtained by distillation of mixture of 19.6 mole % methanethiol (Eastman Kodak Co. white label) in isobutane (Phillips 99.9% pure). The distillation was carried out in standard (Podbielniak) low temperature distillation apparatus, which is equivalent to about 25 theoretical plates, at a reflux ratio of about 50:1. Several cuts were taken after the temperature had leveled out and after intermittent periods of total reflux operation. We estimate that the data are good to ±0.5° and ±0.5 mole %.

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(1) Denyer, Fidler and Lowry, *Ind. Eng. Chem.*, **41**, 2727 (1949).

Eight-membered Carbocycles. IV. Reduction of Cycloöctatetraene

BY L. E. CRAIG, R. M. ELOFSON AND I. J. RESSA

RECEIVED SEPTEMBER 2, 1952

Since it has been shown that cycloöctatetraene can be determined quantitatively by polarographic analysis,[1] the electrolytic reduction of cycloöctatetraene at a mercury cathode was investigated. Reduction was found to proceed smoothly in neutral and alkaline solutions in the presence of the tetramethylammonium ion. Without the tetramethylammonium ion, the reduction was found to be much less efficient, a fact which is in agreement with the polarographic findings.[1]

The product of the electrolytic reduction was shown by elementary analyses and by the absorption of three molar equivalents of hydrogen to give cycloöctane to be cycloöctatriene. Chromatographic examination of the product showed that two materials were present, one to the extent of about three times the other. The ultraviolet absorption spectrum of the material present in the larger amount was essentially identical with that reported by Cope and Hochstein[2] for 1,3,6-cyclooctatriene. The ultraviolet absorption spectrum of the mixture produced by electrolytic reduction indicates that it is a mixture of about 75% 1,3,6-cycloöctatriene and 25% 1,3,5-cycloöctatriene, which is in agreement with the composition indicated by the chromatographic separation.

During the course of the work, isomerization of 1,3,6-cycloöctatriene to 1,3,5-cycloöctatriene during slow distillation was encountered. The alkali-catalyzed isomerization as reported by Cope and Hochstein[2] was confirmed by treating with ethanolic sodium ethoxide and following the isomerization by means of the ultraviolet absorption spectra. The curves of Fig. 2 clearly indicate that the one product is being formed at the expense of the other. It, therefore, seems probable that 1,3,6-cyclooctatriene is the product formed upon electrolytic reduction and that the 1,3,5-cycloöctatriene is formed by isomerization. The formation of bicyclic hydrocarbons in the reduction appears to be negligible because of the high (84%, distilled) yield of cycloöctane obtained on hydrogenation.

Cycloöctatrienes have also been reported to be produced from cycloöctatetraene by the addition of lithium followed by treatment with methanol,[2,3] by reduction with sodium in liquid ammonia,[3] and by reduction with sodium and methylaniline in ether.[4] Ziegler and Wilms[4] suggested that the first product of the reduction with sodium and *m*-ethylaniline in ether is bicyclo[4,2,0]-3,7-octa-

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(1) R. M. Elofson, *Anal. Chem.*, **21**, 917 (1949).

(2) A. C. Cope and F. A. Hochstein, THIS JOURNAL, **72**, 2515 (1950).

(3) W. Reppe, O. Schlichting, K. Klager and T. Toepel, *Ann.*, **560**, 1 (1948).

(4) K. Ziegler and H. Wilms, *ibid.*, **567**, 1 (1950).